

**PURIFICATION PROCESS**

This invention relates to a method for the purification of metal particles, for example, metal powders and other finely sized metal samples, and, in particular, to ones that have been produced by the process of electrochemical reduction of metal compounds. The invention is particularly suited to the purification of titanium powder formed from the electrolytic reduction of titanium oxide  $\text{TiO}_2$ .

WO 99/64638 describes methods for the electrolytic reduction (or "electro-reduction") of metal compounds. Certain embodiments of those methods involve the electrolysis of metal oxides or other compounds in a cell containing a liquid (fused salt) electrolyte and an anode, the metal oxide forming or contacting the cathode. Conditions are controlled so as to bring about the selective dissolution of the oxygen of the cathode in preference to deposition of the metal cation of the fused electrolyte. The metals extracted by such methods, however, often require further purification.

GB2359564 is directed to improved methods for carrying out such processes, particularly to produce powdered titanium, and some of those methods are summarised below:-

Production of powder by reduction of sintered metal oxide granules

Sintered granules or powders of metal oxide can be used as the feedstock for the electrolysis described in the above referenced method, as long as appropriate conditions are present. In one example, powdered titanium dioxide in the form of granules or a powder is used, the powdered particles preferably having a size in the region of  $200\mu\text{m}$ .

As illustrated in Figure 1, the granules of titanium dioxide 1 are held in a basket 2 below a carbon anode 3 located in a crucible 4 having a molten salt 5 therein. These are prevented from sintering together by maintaining particle motion by any appropriate method e.g. in a fluidised bed arrangement. Agitation is provided either by mechanical vibration or by the injection of gas underneath the basket. Mechanical

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vibration can, for example, be provided by ultrasonic transducers mounted on the outside of the crucible or on control rods. The key variables to be adjusted are the frequency and amplitude of the vibrations in order to get an average particle contact time which is long enough to get reduction, but short enough to prevent diffusion bonding of the particles into a solid mass. Similar principles would apply to agitation by the injection of gas, except here the flow rate of the gas and size of the gas bubbles would be the variables controlling particle contact time.

#### Production of powder by deposition of $M_1$ onto the cathode

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If a metal is deposited onto a cathode (based on the electrolytic process previously described) from a second source of the metal at a more positive potential, the resulting metal deposited thereon is dendritic in structure. This is particularly so where the metal is titanium. This form of titanium is easy to break up in to a powder as individual particles are connected together only by a small surface area. This method can be used to produce titanium powder from titania. In this method, illustrated in Figure 2, a second cathode 6 is provided which is maintained at a potential that is more negative than the first cathode 7. When the deposition of titanium on the first cathode has progressed sufficiently, the second electrode is switched on, leading to the dissolution of titanium from the first cathode and deposition 8 onto the second cathode 6 in dendritic form. The other reference numerals represent the same items as in Figure 1.

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#### Use of continuous powder feed

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Continuously feeding a fine powder of metal oxide into the electrochemical cell allows for a constant current and a higher reaction rate. A carbon electrode is preferred for this method. This method permits the use of cheaper feedstock as a sintering and/or forming stage is no longer needed.

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This method is shown in Figure 3 which shows a conducting crucible 1 which is made the cathode containing a molten salt 2 and inserted therein is an anode 3. Titanium dioxide powder 4 is fed into the crucible where it undergoes reduction and is

deposited at the base of the crucible. The thick arrow shows the increasing thickness of the reduced feedstock 5.

5 In electro-reduction methods such as those exemplified above, the purity of the metal powder may be affected by the starting materials and processing parameters used. For example, it has been found that some variations of the method when used to produce titanium powder result in powder that contains "contaminating impurities" resulting therefrom, including light metals such as magnesium or calcium, as well as salts such as calcium chloride (the latter being a preferred electrolyte). Such  
10 impurities are known to affect the mechanical properties of alloyed metal components, for example, salt inclusions are known to affect the fatigue performance and weldability of titanium alloys.

A consequence of the presence of those contaminating impurities in  
15 electrolytically reduced metal powders is that they are unsuitable for use in lower temperature powder metallurgy processes such as sintering or forging which are performed at temperatures below the alloy melting temperature.

In accordance with the present invention there is provided a method for  
20 purifying metal  $M_1$  particles manufactured by an electrochemical reduction process, the method comprising the steps of:

introducing the metal  $M_1$  particles into a heat source at a temperature substantially equal to or higher than the melting point of  $M_1$  so as to cause  
25 vaporisation of some or substantially all of the contaminating impurities present;

removing the vaporised impurities from the vicinity of the particles;

and cooling the purified metal  $M_1$  particles.

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The present invention thus provides a method for purifying electrochemically reduced metal particles so as to reduce or remove the aforementioned "contaminating impurities" introduced by the reduction process, so as to enable, for example, direct

use of the electrolytically reduced metals in lower temperature powder metallurgy processes.

It has been found that the kinds of impurities introduced by such electro-  
5 reduction processes are usually more volatile than the metal  $M_1$  and may be  
conveniently removed by the present process. Such impurities may comprise light  
metals, for example, calcium and magnesium, as well as salts from the electrolyte,  
such as calcium chloride. For effective removal of impurities without significant loss  
of metal  $M_1$ , the impurities should preferably be more volatile than the metal  $M_1$  by at  
10 least a factor of ten, or preferably 20, in terms of their respective vapour pressures at  
the processing temperature. Preferably, the processing temperature and/or heating  
time should be sufficient to remove substantially all the contaminating impurities, for  
example, so as to reduce their total level to less than 50 ppm, or less than 10% their  
initial total concentration. Preferably the process is conducted so that there is little or  
15 no evaporation (for example, less than 5%) of the metal  $M_1$ .

Another feature of metal powders produced by electrolytic reduction of oxide  
or oxides is that the powder particles tend to be irregular in shape, contain internal  
cavities and have a rough outer surface. For certain powder metallurgy processes  
20 these features are undesirable, and a fully dense spherical particle morphology is  
preferred, for example in order to impart good flowability. Hence, although the  
particles may only be partially melted in order to remove said impurities, in most  
cases the particles need to be fully melted to achieve dense, spherical particles.

25 Desirably, the heat source is arranged such that the metal particles may be  
allowed to free fall through the heat source. Suitable heat sources include but are not  
strictly limited to a hot plasma torch, a hot gas flame, a tube furnace, an induction  
coil, electric arcs and lasers.

30 In one embodiment of the invention, the particles may be blown through a  
plasma torch into the flame and allowed to free fall into a collecting vessel. The torch  
is preferably arranged at a sufficient height above the vessel such that any portion of  
the particles that is melted by the heat source is substantially solidified before

collection. This prevents distortion of the shape of the particles.

In another embodiment the established method of levitation melting may be used to hold particles of powder in a surrounding heat source for a period sufficient to vaporise the impurities. In a further embodiment, zero gravity processing may be used. The common purpose of these embodiments is to suspend the particles individually in mid-air, out of contact with any surfaces, so as to enable particles to be heated and melted and resolidified individually, without contact with each other, or a container.

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The temperature of the heat source should be at or above the melting point of the metal  $M_1$ . For titanium the desired point is about 1680°C and for titanium alloys approximately 1500-1800°C. It is known that an argon or helium arc plasma torch can achieve temperatures sufficient to melt titanium powder particles entrained in the flame. Ideally, the process is conducted in a controlled atmosphere, for example, at low pressure/vacuum and/or in an inert atmosphere. In the case of Ti it is important that the powder particles are kept separate from oxygen or nitrogen while above a temperature of about 500°C. This is achieved in practice either by processing in a vacuum or in an atmosphere of Ar.

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The method is applicable to all metals and alloys provided a temperature sufficient to melt the particles and volatilise the contaminants can be achieved.

The step of removing the impurities may simply involve allowing them to be swept away by the gas flow from the flame of the heat source. Preferably, the step of removing the impurities involves condensing the vaporised impurities on cold collector plates positioned adjacent the hot gas flame and disposing of the condensed impurities. Additionally, if the contaminants re-condense onto the surfaces of the powder particles  $M_1$ , then they can be removed easily with a water or dilute acid wash.

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Aside from improving the purity of the metal powder, the inventors have appreciated that by exposing small particles of a metal  $M_1$  to a heat source at around

or above the melting point, but below the boiling point of  $M_1$ , and allowing them to fall freely through the heat source, the shape of the particles can be altered to a near spherical shape. Spherical particles provide improved bonding in powder metallurgy processes. Thus it is preferred that the temperature of the heat source used in the  
5 purification process of the method is substantially equal to or higher than the melting point of  $M_1$  but lower than the boiling point of  $M_1$ .

Powdered particles purified in accordance with the method of the invention may be used in the formation of alloy metal articles made by various powder  
10 metallurgy methods and will provide improved particle bonding and mechanical properties in the alloyed article.

In another aspect, the invention provides a method for the manufacture of a metal alloy article containing a metal  $M_1$ , comprising the steps of:  
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electrochemically reducing a source of a compound of the general formula  $M_1X$  to remove substantially all of element X and provide powder particles consisting substantially of metal  $M_1$ ;

20 introducing the metal powder  $M_1$  into a heat source at a temperature substantially equal to or higher than melting point of  $M_1$  for a period of time sufficient to cause vaporisation of a significant proportion of the one or more impurities;

removing the vaporised impurities;  
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cooling the purified metal  $M_1$  powder; and

mixing the purified  $M_1$  powder with powder of other alloy components and, optionally, performing a powder metallurgy process on the mixture to form the  
30 alloyed article.

Preferably, the temperature of the heat source will be substantially equal to or above the melting point of the metal  $M_1$ .

The electrochemical reduction method may comprise any suitable electro-reduction method for the production of metal particles, and includes the methods described herein or as described in WO 99/64638.

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The powder metallurgy process used may be any conventional powder metallurgy process including but not limited to powder sintering and/or forging. One example of such a process is hot isostatic pressing.

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Purified powders made according to the first aspect of the invention may be used in various other processes for the manufacture of metal articles where powdered starting materials are desirable.

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For the purposes of this specification  $M_1$  may be construed to mean a single metal or a combination of different metals formed in a single method. References to particles may be construed to mean a powder or other finely sized metal samples, for example, granules or pellets, that could be purified by the present method. A powder may be construed to comprise small particles up to about 1mm in diameter.

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In another aspect, the inventors have found that sheets, or other shapes of metals produced by the previously described electrochemical reduction methods, may also be purified through the application of heat at a temperature equal to or higher than the melting point of  $M_1$  for a period sufficient to cause vaporisation of a significant proportion of the one or more impurities. In order to benefit fully from this inventive method, the sheet or other shape of metal product  $M_1$  desirably has at least one dimension that is less than or equal to about 1mm in size.

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In a further aspect, there is provided a method for purifying metal  $M_1$  particles manufactured by an electrochemical reduction process, the method comprising the steps of introducing the metal  $M_1$  particles into a heat source at a temperature substantially equal to or higher than the melting point of  $M_1$  so as to melt the particles and cause substantially all the contaminating impurities to separate out from the metal into a separate phase, cooling the metal  $M_1$  particles, and removing any impurities

that are still in the vicinity of the particles. For example, where lower temperatures are employed the impurities may merely separate out into a separate liquid phase on the surface of the molten particles, rather than vaporise, and may subsequently be removed, for example, by a washing step.

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Examples employing the present invention will now be described in more detail, by way of example only, with reference to the accompanying drawings of which:

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Figure 1 shows a prior art electrolytic cell in which the metal oxide to be reduced is in the form of granules;

Figure 2 shows a prior art electrolytic cell in which an additional cathode is provided in order to refine the metal to a dendritic form;

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Figure 3 shows a prior art electrolytic cell employing a continuous powder feed;

Figure 4 shows a preferred purification apparatus according to the present invention;

Figure 5 shows an alternative purification apparatus according to the present invention;

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Figure 6 shows a schematic illustration of an apparatus for the production of titanium metal or alloy sheet; and,

Figure 7 shows a schematic illustration of an apparatus for the production of titanium metal or alloy bar stock.

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Figures 1 to 3 show, by way of example, three suitable prior art arrangements for producing metal powders by electrolytic reduction, and are discussed in more detail above.

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Figure 4 shows a preferred arrangement for purifying a powder in which the particles are blown through a plasma torch into a flame and allowed to free fall into a collecting means. The reactor 10 comprises a large metal vessel 11, provided with an inert atmosphere 12, which is preferably argon dispensed from jets 9. For titanium, the process should be entirely contained in a metal vessel in an inert gas atmosphere.



The metal particles ( $M_1$ ) enter the vessel from a supply hopper 14 through the plasma torch 13, which is attached and sealed to the top of the vessel 11 so that it points downwards, and provides sufficient heat to melt and vaporise the metal particles and contaminants, respectively, as they pass through the upper section of the vessel 11.

5 The torch 13 is preferably arranged at a sufficient height above the collecting means that any portion of the particles that is melted by the heat source is substantially solidified before collection. This prevents distortion of the shape of the particles. The re-solidified powder is collected and sealed into a metal collection hopper 15 via a funnel cyclone collector 16.

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In the alternative embodiment shown in Figure 5, levitation melting is used to hold particles of powder in a surrounding heat source for a period sufficient to vaporise the impurities. The apparatus comprises a supply hopper 14 through which metal particles ( $M_1$ ) enter via a valve 24 into a large ceramic tube-like chamber 23.

15 The powder is allowed to fall through the ceramic tube under its own weight. Around the mid-section of the chamber 23 is an external concentric electromagnetic induction coil 22, which both heats and levitates the metal powder particles such that they spend sufficient time at a suitable temperature for volatile contamination removal and spheroidisation to take place. The purified powder then falls to the bottom of the chamber 23, cooling sufficiently to solidify, before exiting via valve 25 and being collected and sealed into a metal canister 15. In a further refinement, an inert gas flow is introduced counter to the direction of the metal powder flow via inlet 21 and outlet 20, and this both enhances the cooling of the powder particles at the lower end of the tube, and also helps to carry away volatile species.

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An electro-reduction process, also known as an electro-deoxidation (EDO) process, is less expensive and easier to perform than conventional metal extraction methods. Metal particles produced by an EDO process may advantageously be used directly as feedstocks in manufacturing processes that incorporate the present purification process as an integral stage.

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Thus, the present invention further provides a method for the manufacture of a metal alloy article of uniform cross section comprising the steps of:

introducing a continuous source of metal alloy  $M_1$  pellets, manufactured by an electrochemical reduction process, to a processing means;

heating the pellets as they approach the processing means, by free-fall through a heat source, to a temperature substantially equal to or higher than the melting point of  $M_1$  so as to cause vaporisation of some or substantially all of the contaminating impurities present;

removing the vaporised impurities from the vicinity of the pellets;

drawing the metal through the processing means so as to coalesce the pellets to form the desired article; and,

cooling the cast stock.

Such a manufacturing process has, in particular, significant benefits over conventional processes for the production of titanium articles. Conventional methods for the manufacture of titanium and titanium alloy stock involve hot working of large titanium alloy ingots. The high temperatures and pressures required for these processes contribute to the high cost of this stock compared to other metal products such as steel and aluminium alloys. Titanium is conventionally obtained from its ore by the Kroll route, a complex chlorination and magnesium reduction method. The purified metal granules, called sponge, are then melted with the alloying additions and cast into large titanium alloy ingots. The metal is melted at least twice and sometimes more, in order to ensure chemical homogeneity and freedom from defects. The large titanium alloy ingots are then hot forged repeatedly to produce the semi-finished alloy stock shapes, such as bar, plate, sheet and wire, required for the manufacture of articles.

The present invention aims to provide novel methods for the manufacture of titanium or other metal alloy stock, which are less expensive and easier to perform.

For sheet production, the above-mentioned manufacturing process incorporating the purification stage may involve:

introducing the continuous source of pellets of the metal alloy to a pair of cooled feed rollers;

heating and simultaneously purifying the pellets in the above described

manner as they approach the nip of the pair of feed rollers;  
drawing the metal through the nip of the rollers to form a sheet of metal alloy;  
and,  
cooling the sheet.

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The pellets should be heated sufficiently to allow them to coalesce to form a sheet when subjected to the pressure of the nip, and may be heated so that they soften, or, at least partly melt, or even fully melt. The term "pellet" covers particles ranging from powders to granules.

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Preferably either or both of the feed rollers are water cooled by passing a coolant through their centres. One suitable coolant is water, other suitable fluids will no doubt occur to the skilled addressee.

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Alternatively, for stock production, the above-mentioned manufacturing process incorporating the purification stage may involve:

introducing the continuous source of pellets of the metal alloy to a shaped crucible;

heating and simultaneously purifying the pellets in the above described  
manner as they approach the exposed surface of the crucible;

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drawing the at least partially molten metal from an opposing surface of the crucible through a die, the die having a cross section of near net shape and dimensions to the desired net shape and dimensions of the required stock; and  
cooling the cast stock.

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The sheet or cast stock may be allowed to cool or may be actively cooled.

The alloy pellets may be obtained by an electro-deoxidation process such as that described in WO 99/64638, or, in the Applicant's co-pending applications  
GB2359564 or GB2362164. As is described in the above specifications,  
electrochemical reduction may be used to provide small pellets of alloy having high purity and good grain structure. Thus, heating and purification involving softening or partially melting the pellets is sufficient to bond the pellets and obtain a mass of alloy

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having good mechanical properties.

The step of heating the pellets is preferably carried out by means of an energy beam. The energy beam may, optionally, be selected from an electron beam, a laser or  
5 a plasma torch.

Preferably, the processing temperature and/or heating time should be sufficient to remove substantially all the contaminating impurities, for example, so as to reduce their total level to less than 50 ppm, or less than 10% their initial total concentration.  
10 Preferably the process is conducted so that there is little or no evaporation (for example, less than 5%) of the metal. Ideally, the process is conducted in a controlled atmosphere, for example, at low pressure/vacuum and/or in an inert atmosphere. In the case of Ti it is important that the powder particles are kept separate from oxygen or nitrogen while above a temperature of about 500°C. This is achieved in practice  
15 either by processing in a vacuum or in an atmosphere of Ar. The use of argon or helium arc torches is particularly preferred.

In either method, the rolled or cast stock may be further processed, for example, by one or more additional intermediate steps such as further working or heat  
20 treatments of the stock, prior to final cooling. Products of the methods are comprised of fully dense metal alloy. The homogeneity of the final metal is improved considerably because the pellets are provided via an electrochemical reduction method, as compared to the alternative of using Kroll sponge and powder or particles of the alloy additions. The present methods require considerably less cumbersome  
25 and costly apparatus compared to conventional methods where the starting materials are introduced to the casting or rolling apparatus fully molten and are particularly suited to the production of small quantities of stock where mechanical properties and metal homogeneity are of importance.

30 The present methods are particularly suited to the manufacture of low volume or small size products, which could be prohibitively costly to produce by conventional methods.

Two embodiments illustrating the roller and crucible based processes will now be further described with reference to Figures 6 and 7.

As can be seen from Figure 6, pellets of titanium metal or alloy 31 are delivered through a hopper 32 to a pair of counter-rotating feed rollers 33a, 33b. The rollers are cooled by a water-cooling system (not shown). An energy beam 34 is arranged to concentrate a beam of energy along a line just above the nip of rollers 33a, 33b and causes at least partial melting of the pellets seated on and between the rollers. As the rollers 33a, 33b rotate, the at least partially melted pellets are drawn into the nip and are squeezed together to form a solid mass of the titanium or titanium alloy in the form of a sheet 35. The hot sheet falls to a conveyor 36 and is carried away for further processing and/or cooling.

Figure 7 illustrates a similar arrangement for the production of bar stock having a square cross-section. A source of pellets 41 is delivered through a hopper 42 to a shallow crucible 47. A laser 44 is mounted on a track 48 along which the energy beam sweeps back and forth. The energy beam is aimed at the top surface of the crucible 47 and causes at least partial melting of the pellets 41 delivered thereto. The metal is drawn through a square shaped die 49 communicating with a lower surface of the crucible 47 and bar stock 45 of the titanium or titanium alloy emerges. The bar stock may be cut to length by a cutter (not shown). The bar stock is collected by a conveyor system 46 and removed for cooling and/or further processing.

The parameters for a method carried using either of the described apparatus are more generally described below.

The feedstock in the form of pellets (including powder or granules) is stored inside a hopper that is an integral part of a vacuum chamber housing the roller and for example, E-beam (electron-beam) or a laser beam melting assembly. During operation the feedstock is poured over the rollers at a controlled rate using a regulator valve attached to the feeder. The vacuum chamber is desirably at a pressure ranging from  $1 \times 10^{-6}$  to  $1 \times 10^{-5}$  mBar during the operation.

The energy beam directed at the pellets heats and at least partially melts the titanium feedstock between the roller gap, which either softens it sufficiently for it to be deformed and consolidated as it passes through the roll gap, or melts it then solidifies it instantaneously on contacting the rollers and also gets deformed into a strip subsequently. The temperature of the solid strip coming out of the rollers is in the region of 600°C. Several titanium strips of dimensions in the range 300-900 mm (length) x 60-100 mm (width) x 3.0 mm (thickness) have been produced using this method.

This method is not specific only to titanium feedstock, it has potential application for direct production of strips of any metallic powder, and especially those that are very sensitive to the absorption of impurities such as oxygen or nitrogen.

The method of manufacture of strip described above is ideally suited to feed stock of uniformly sized granules of less than about 1 mm dimensions. Larger granules may be optimal for production of thicker sheets by this method.

Rollers are desirably cooled through the centre. The primary requirement is that the chamber housing the rollers should be in a vacuum (or very low pressure environment) to stop the molten titanium from picking up oxygen. A water-cooled roller assembly has been developed by the applicants that lets the water flow through the rollers and bearings, while maintaining good vacuum tightness.

For both variants of the invention described here for the production of metal alloy sheet and the production of shaped bar stock by energy beam heating of pellets or granular feed, the heating is conducted so as simultaneously to remove all or part of any volatile contamination that may be present in the feed material, for example, EDO granules may contain contaminants such as calcium chloride, calcium oxide or calcium metal.